

POLYMERS FOR SPACECRAFT HARDWARE
MATERIALS SPECIFICATIONS AND ENGINEERING INFORMATION

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SCOPE

This report covers the work performed during the period February 10, to March 9, 1966 on "Polymers for Spacecraft Hardware--Materials Specifications and Engineering Information," SRI Project ASD-5046 under JPL Contract No. 950745.

The primary objectives of this program are to assist the Jet Propulsion Laboratory of the California Institute of Technology in the development and preparation of polymeric material specifications to be used in connection with JPL spacecraft, and to provide a study of the effects of simulated space environment on selected commercial polymeric products. The materials and products to be studied and the extent of work to be performed are specified by the JPL Cognizant Engineers.

The program is conducted as two interrelated and concurrent phases: The purpose of Phase I, Polymeric Materials Specifications, is to obtain quantitative values for parameters which may be used to assure the performance of a given batch of material in a spacecraft environment. The purpose of Phase II, Engineering Information, is to establish material limitations and to obtain detailed design information.

Since a variety of activities and materials are involved in the overall program, an outline of the work performed and contemplated is given at the beginning of the reports for each Phase.

INTERIM REPORT

In view of the broad scope of this program and its many activities, the issue of a report which summarizes the past six months of effort is most appropriate and is mutually agreeable with JPL and SRI personnel. Thus, Interim Report No. 2 is being prepared for issue before the end of March.

PHASE I - POLYMERIC MATERIALS SPECIFICATIONS

WORK PERFORMED

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Chemical Tests

Physical Tests

Thermal-Vacuum Weight Loss

WORK PERFORMED

Chemical Tests

RTV Silicones

Work has been completed for a series of chemical test methods for RTV-silicone potting-compound base materials. The results obtained for hydroxyl content of RTV-11, -60, -560, and -615A are given in Table I. A review of the literature indicated that a number of procedures had been suggested for determination of the silanol group but that most of them do not provide satisfactory and reproducible results. One of the more promising suggestions, involving the distillation of the water of condensation of silicones, was briefly investigated but insufficient water was obtainable even with 100-g samples. Thus, the ASTM procedure, ASTM E 222-63T, "Hydroxyl Groups by Acetic Anhydride Acetylation," was used to obtain the results given in Table I:

The sample is refluxed with a solution of acetic anhydride in pyridine, excess reagent is hydrolyzed with water, and the acetic acid is titrated with standard sodium hydroxide solution. A potentiometric titration was used for this work.

Hydrolyzable halide was determined for RTV-615B, which contains the curing agent for 615A in a silicone base; as shown in Table I, the halide content is extremely low, or absent.

Epoxy-Silver Solder Paste

Determinations have been completed for meaningful properties of Eccobond 56C/11, a silver-filled-epoxy solder paste (Emerson and Cuming, Inc.), and the results are summarized in Table II. The methods for hydrolyzable halide content, epoxy equivalent, and filler content have been described previously and are incorporated into JPL specifications test methods for epoxy adhesives.

Table I				
RESULTS OF DETERMINATIONS OF GENERAL ELECTRIC SILICONE POTTING COMPOUNDS				
Material	Hydroxyl Content, m.e./g	Density ₄ ²⁵ g/ml	Hydrolyzable Halide, wt-%	Shore Hardness*
RTV-11	0.98-1.10	1.161-1.168		55
RTV-60	0.27-0.36	1.476-1.488		60
RTV-560	0.19-0.26	1.419-1.425		64
RTV-615A	0.02-0.05	1.013-1.015		50
RTV-615B		1.002-1.003	< 0.001	

* cured material

Table II	
RESULTS OF DETERMINATIONS OF ECCOBOND 56C/11*(Emerson and Cuming, Inc.)	
Property	Values
Epoxy equivalent (g sample/g-equiv. of epoxy)	1,099-1,109
Hydrolyzable halide	< 0.01 %
Filler content (silver)	79.61-79.92 wt-%
Nonvolatile content	99.54-99.62 wt-%
Infrared absorbance	(curve prepared)

* Batch No. 324

Polyurethanes

The literature search has been completed for analytical procedures for the properties of polyurethanes which are most meaningful for specifications purposes. Work is in progress on the evaluation of procedures for hydroxyl content, isocyanate content, hydrolyzable halide content, and filler content. Two typical candidate materials for spacecrafts are

being used for this work: a 2-part coating material and a 2-part foamed-in-place material.

Physical Tests

RTV Silicones

The densities of the silicone base materials, reported in Table I, were determined in accordance with ASTM Method D 1875-61T. Weight-per-gallon results were converted to densities at 25/4, in keeping with the JPL specifications format; all results are in excellent agreement with manufacturer's specifications.

ASTM slabs of the silicone potting compounds (RTV-11, -60, -560, and -615) were prepared according to manufacturer's instructions for mixing and curing:

- RTV-11: 90 g base mixed with 0.5% catalyst T-12; evacuated for 30 minutes, then poured into mold and allowed to stand at room temperature for 48 hours before removal.
- RTV-60: 90 g base mixed with 0.5% catalyst T-12; evacuated 30 minutes before mixing with catalyst, evacuated 60 minutes after mixing with catalyst, evacuated 30 minutes after pouring in mold, and allowed to stand 48 hours in mold before removal.
- RTV-560: 90 g base material with 0.5% catalyst T-12; evacuated 2 hr before mixing in catalyst, evacuated 2 hour after mixing in catalyst, evacuated 1 hour after pouring in mold, and allowed to stand 72 hour in mold before removal.
- RTV-615: Mixed 10 parts A to 1 part B; evacuated 30 minutes before adding part B, evacuated 30 minutes after mixing, evacuated 45 minutes after pouring, and allowed to stand 96 hours before removal from mold.

Shore hardness tests of the elastomers were conducted according to ASTM Method D-676; the results given in Table I are an average of 5 readings.

Epoxy-Silver Solder Paste

Determinations for nonvolatile content of Eccobond 56C/11 were made in accordance with ASTM Method D 1259-61(B); the results are given in Table II.

An infrared absorbance curve was obtained for a film of the resinous material; the film was prepared by evaporating an acetone extract of the epoxy-silver paste on an optical salt flat. The curve will be published in a formal report; a duplicate curve was prepared for incorporation into specifications.

Polyurethanes

Work is in progress for the determinations of physical properties of typical polyurethane materials. The tests include determination of density and nonvolatile content, and the preparation of infrared absorbance curves.

Thermal-Vacuum Weight-Loss Determinations

Polyvinylfluorides

Vacuum-weight-loss determinations by the standardized procedure have been made for two polyvinylfluoride films, candidates for structural and insulation applications in spacecrafts: Tedlar-200BG30WH and Tedlar-100BG30TR (DuPont). Tedlar-100BG30TR is a "pure" transparent film and Tedlar 200BG30WH is a filled material. Weight-loss results for the filled material are somewhat higher than for the unfilled as shown in Tables III and IV, but both are within the lower limits for suitable polymeric materials:

Tedlar 200BG30WH	$0.17\% \pm 0.05$ @ 48 hr
Tedlar 100BG30TR	$0.08\% \pm 0.02$ @ 48 hr

It is interesting to note, however, that both materials are subject to thermal-forming, i.e., flat films rolled for insertion in the sample chambers tended to maintain the roll curvature after removal from the thermal-vacuum environment.

Table III WEIGHT-LOSS DATA FOR PVF FILM DU PONT TEDLAR 200BG30WH (125°C and 10 ⁻⁶ torr)			
Time, Hrs.	S. Wt., g	Wt. Loss, g.	Wt. Loss, %
48	1.0121	0.0019	0.19
	1.0012	0.0015	0.15
96	1.0073	0.0015	0.15
	0.9873	0.0015	0.15
192	1.0034	0.0016	0.16
	1.0066	0.0015	0.15

Table IV WEIGHT-LOSS DATA FOR PVF FILM DU PONT TEDLAR 100BG30TR (125°C and 10 ⁻⁶ torr)			
Time, Hrs.	S. Wt., g	Wt. Loss, g	Wt. Loss, %
48	1.0621	0.0009	0.08
	1.0633	0.0009	0.08
96	1.0692	0.0010	0.09
	1.0319	0.0008	0.08
192	1.0569	0.0008	0.08
	1.0402	0.0007	0.07

Polyphenyl Ether

Weight-loss determination was also made for a polyphenyl ether coating material, Doryl B-109-4 (Westinghouse). The material was applied to a copper coil, as described previously, and cured for 2 hours at 250°C in accordance with manufacturer's directions. The results obtained, summarized in Table V, indicate that this material is not suitable for space-craft use, at least under recommended curing conditions.

Table V WEIGHT-LOSS DATA FOR COATING WESTINGHOUSE DORYL-B-109-4 (125°C and 10 ⁻⁶ torr)			
Time, Hrs.	S. Wt., g	Wt. Loss, g	Wt. Loss, %
48	0.5460	0.0094	1.72
	0.5798	0.0105	1.81
96	0.5610	0.0172	3.07
	0.6534	0.0165	2.53
192	0.6742	0.0238	3.53
	0.5903	0.0220	3.73

Polyfluorocarbons

Although many creditable publications have referred to the superior thermal-vacuum weight-loss characteristics of polyfluorocarbons, it was nevertheless considered appropriate to determine the values for at least two representative materials in order to complement the systematic survey being undertaken for candidate spacecraft materials.

The data given in Tables VI and VII for Teflon TFE and FEP (du Pont) clearly confirm the superiority of these materials, as far as weight-loss criteria is concerned.

Table VI WEIGHT LOSS DATA FOR DU PONT TEFLON FEP TYPE A (5 mil) (125°C and 10 ⁻⁶ torr)			
Time, Hrs.	S. Wt., g	Wt. Loss, g.	Wt. Loss, %
48	0.7515	0.0000	0.000
	0.6974	0.0001	0.014
96	0.6666	0.0001	0.015
	0.5448	0.0002	0.040
192	0.7344	0.0005	0.068
	0.7121	0.0002	0.028

Table VII WEIGHT LOSS DATA FOR DU PONT TEFLON TFE 100A (20 mil) (125°C and 10 ⁻⁶ torr)			
Time, Hrs.	S. Wt., g	Wt. Loss, g	Wt. Loss, %
48	1.1549	0.0001	0.009
	1.1367	0.0001	0.009
96	1.2564	0.0004	0.003
	1.3450	0.0004	0.002
192	1.2752	0.0005	0.004
	1.2365	0.0003	0.002

FUTURE WORK

Chemical Tests

Determinations of the chemical properties of polymers will be continued as required for incorporation into specifications requirements and test procedures. Work will continue toward completion of chemical test methods for polyurethanes.

Physical Tests

Work will continue toward completion of physical tests for RTV-silicone potting compounds and for polyurethanes.

Thermal-Vacuum Weight Loss

Vacuum weight-loss determinations by the standardized procedure will be made on a continuing basis in order to establish limitations for specifications requirements for various polymeric materials.

PHASE II - ENGINEERING INFORMATION

WORK PERFORMED

Volatile Condensable Material

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Volatile Condensable Material

Mechanical Properties

Physical Properties

WORK PERFORMED

Volatile Condensable Material

Micro-VCM

The micro-VCM apparatus is now being operated on a routine basis. The source of error for the abnormal range of blank collector-plate weights of ± 50 micrograms (see Monthly Report No. 20) was easily identified with the porous soft solder used to fasten the holding screws to the plates; the soft solder has been replaced with silver solder, and blank weights are now in a reasonable and reproducible range of ± 10 micrograms.

In general, duplicate determinations for both weight-loss and VCM values average about $\pm 0.06\%$ (abs.). As shown in Table VIII, repeated determinations for the same material may show a variation of $\pm 0.2\%$ (abs.), which is quite adequate for screening. Control samples will be run with each set of determinations as indicators of system performance; since the SE-555(white) sample is depleted, it is being replaced with SE-555(gray) a similar material.

Table VIII				
MICRO-VCM DETERMINATIONS OF CONTROL SAMPLES (24 hr at 125°C and 10^{-6} torr) (VCM collector plates at 25 °C)				
Run No.	Material	Total Wt. Loss, %	VCM wt-%	Noncondensable Wt. Loss, %
1	SE-555(white)	0.29	0.22	0.07
		0.41	0.28	0.13
2		0.78	0.43	0.35
		0.72	0.42	0.30
3		0.57	0.32	0.25
1	Viton A 4411A-990	0.49	0.01	0.48
		0.53	0.09	0.44
2		0.55	0.01	0.54
		0.63	0.02	0.61
3		0.51	0.00	0.51

The first set of results for a series of polymeric materials is summarized in Table IX. The values obtained for weight-loss agree within 0.2% of those obtained by the standardized weight-loss procedure. Maximum VCM values for SE-555(white) and Viton-990 (see Table VIII) and SE-555(gray) (see Table IX) agree favorably with those obtained at 48 hours (maximum) in the prototype VCM apparatus:

<u>Material</u>	<u>Prototype VCM-Value</u>	<u>Micro-VCM-Value</u>
SE-555(white)	0.56%	0.28% (av)
SE-555(gray)	0.40	0.30 (av)
Viton-990	0.05	0.02 (av)

Exact duplication of former results was not anticipated because of the different areas used for VCM collection. In the micro-VCM apparatus, all VCM is collected directly on a collector plate of approximately twice the surface area used in the prototype apparatus. The increased surface area permits volatilization of material at a greater rate and thus the residuals on the micro-VCM collecting plates would have a slightly different composition than in the prototype apparatus; nevertheless, a factor of two difference is observed.

An illustration of the effectiveness of the micro-VCM procedure for screening is illustrated by the results for Nordel-115: VCM values were determined previously* at 143°C and 93°C for 24-hour periods, with resulting values of 2.0% and 0.3%. A straight line can be drawn between these points, since the VCM value is a function of the rate of evaporation at a given temperature, and a value of 1.4% can be estimated for VCM at 125°C; the micro-VCM value is 1.3%.

The maximum value for VCM at 143°C after 330 hours, for Nordel-115, was about 3.0%. Thus, a maximum value for VCM at 125°C can be estimated as 2.0%. In this comparison, the micro-VCM value of 1.3% for maximum-VCM may appear to be a little low, but it is in keeping with the differences

* Muraca, R. F., et al., Stanford Research Institute, Interim Technical Report No. 2, Project 4257, May 1965.

Table IX					
MICRO-VCM DETERMINATIONS ^a (24 hr at 125°C and 10 ⁻⁶ torr) (VCM collector plates at 25°C)					
Material	Mfr ^b	Total Wt Loss, %	VCM, Wt-%	Noncondensable Wt-Loss, %	Notes ^c
Enjay Butyl EX-1090	ECC	0.80	0.24	0.56	1,3
Enjay Butyl EX-1091	ECC	0.70	0.20	0.50	1,3
Enjay Butyl EX-1092	ECC	0.86	0.10	0.76	1,3
SE-555(gray)	GE	0.53	0.30	0.23	1,2
Hycar-520-67-108-1	BFG	1.90	0.17	0.73	1,2
JPL-1001	AA	0.20	0.10	0.10	1,4
JPL-1002	AA	0.19	0.03	0.16	1,4
Lexan 100-111	GE	0.06	0.02	0.04	1,2
Lexan 101-111	GE	0.08	0.01	0.07	1,2
Lexan 101-112	GE	0.09	0.04	0.05	1,2
Lexan 103-112	GE	0.08	0.00	0.08	1,2
Micarta H-2497	WE	0.18	0.00	0.18	1,2
Micarta 65M25	WE	0.43	0.00	0.43	1,2
Nordel A-5411A-115	DuP	1.80	1.29	0.51	1,5

a) Values are average of 2 determinations: for duplicate samples, VCM and wt-loss may vary $\pm 0.06\%$ abs.

b) ECC, Enjay Chemical Company GE, General Electric Company
 BFG, B. F. Goodrich Company WE, Westinghouse Electric Company
 AA, Ablestik Adhesive Company DuP, E.I.DuPont de Nemours Co., Inc.

- c) 1. Conditioned in 50% humidity for 24 hr before initial weighing, and stored in desiccator for 30 minutes before final weighing.
2. Sample used as received.
3. Postcured 4 hr at 105°C.
4. Postcured 18 hr at 174°C.

anticipated for reasons described above, and it still indicates the unsuitability of this material for spacecrafts.

VCM

Work is well underway toward the design and construction of the vacuum system and support fixtures for the clam-shell units which will be used to provide engineering information on the deposition and subsequent evaporation of VCM. The basic system has been designed and a request for equipment purchases has been prepared.

Volatile Material

Mass Spectrometry

Mass spectrometric identification has been completed of substances volatilized from polymeric materials which have been examined previously for VCM content: Hypalon A-2211A-2718 and Viton A-4411A-990. Volatile material from Hypalon-2718 consisted primarily of water, with small amounts of sulfur dioxide, phthalic acid ester, carbon dioxide, hydrochloric acid, and unsaturated hydrocarbons. Volatile material from Viton-990 was primarily water and solvent (benzyl ether), with small amounts of carbon dioxide, dioctylphthalate, and fluorocarbons. Details of these analyses are given in Interim Report No. 2, to be issued.

Mechanical Properties

Six-Week Storage Tests

Current in situ tests of the effects of the thermal-vacuum environment on the mechanical-property behavior of elastomers SE-3813 and Hycar 520-67-108-2, and plastic polyphenylene oxide (PPO) will be concluded on or about March 17. Preliminary examination of the results obtained from these studies thus far indicate that Hycar-2 is cross-linking at a higher rate than either Hycar-1 or -3. The PPO samples, under a constant load of 2,000 psi, appear to be withstanding the environment. One of our specimens ruptured at about 500 hours; almost no deformation of the surviving specimens has occurred.

Preliminary constant-load tests of polysulfone film, P-2300(GE), are being conducted in air at 125°C. Loads in excess of about 1500 psi appear to cause rupture within 48 hours. After exposure of about 48 hours at 125°C, the polysulfone film appears to have become quite brittle and breaks easily on bending.

Eight-Month Storage Tests

During the past 4 weeks of storage at constant strain in an environment of 125°C and $<10^{-6}$ torr, no samples have ruptured, elastomers being examined are General Electric SE-3604 (silicone), Du Pont Viton A 4411A-990 (vinylidene fluoride-hexafluoropropylene), and Goodrich Hycar-1 (polyacrylic-nitrile). As of this reporting period, 10 weeks of storage have been completed; five samples ruptured during outgassing at 40°C (SE-3604 and Viton A 4411A-990 at maximum strain) and 3 samples ruptured during the first week at 125°C (Hycar-1 at maximum strain).

Work has been completed on the fabrication of the constant-load test apparatus which has been designed for observation of changes in the properties of plastic materials which are subjected to long-term storage in the environment of 125°C and $<10^{-6}$ torr. The apparatus has been installed in the fourth unit of the long-term-storage test system described and illustrated in Monthly Report No. 19.

Eight-month constant-load tests of polyphenylene oxide film have been initiated. Two specimens are being subjected to a load of 1500 psi, four are at 1750 psi, and two are at 2000 psi; several unstrained specimens are also being stored within the thermal-vacuum environment. Load was applied, and evacuation commenced at room temperature on March 2, 1966; the temperature was increased to 45°C on March 3 and held until March 7, at which time the temperature was again increased, with 81 hours being required to reach test temperature of 125°C. The starting time at 125°C for this test is 5:00 p.m., March 10, 1966.

FUTURE WORK

Volatile Condensable Material

Work will continue on the fabrication and assembly of the system for VCM determinations to be made in the clam-shell units for engineering information.

Determinations will be made on a continuing basis for micro-VCM and weight-loss in the micro-VCM apparatus; samples will be selected to meet the requirements of both phases of the program.

Mechanical Properties

Work will continue on the measurements of stress-relaxation changes for selected polymers during a 6-week exposure to the thermal-vacuum environment.

Regular observations will be made of the status of the elastomers which are stored in the thermal-vacuum environment under constant strain for 8 months and the plastic which is stored under constant load for 8 months. Design drawings for the constant-strain apparatus will be published in the forthcoming Interim Report.

Physical Properties

Work will continue as pertinent on the spectral studies of selected polymeric materials which have been exposed to the thermal-vacuum environment.